Studies on the Electrical and Optical Properties of Thin Films of Copper Tellurides

Synopsis of the thesis submitted to
Madurai Kamaraj University
for the award of Degree of
Doctor of Philosophy

by

K.Neyvasagam

Department of Microprocessor and Computer
School of Physics
Madurai Kamaraj University
Madurai - 625 021, India.

April 2008

Synopsis

1 Introduction

Thin film technology is one of the oldest arts and of the newest sciences. Earlier, it was used to decorate statues, windows, walls etc. Integrated circuits are direct applications of thin films[1]. Thin film science has grown into major research area world-wide. Applications of thin films in different fields and synthesis of new materials for industries have resulted in tremendous increase of innovative thin film technologies. Currently, these devolvements go hand-in-hand with the explosion of scientific and technological break through in micro-electronics, optics, and nanotechnology etc. A thin film is two dimensional in its macroscopic appearance as its thickness is negligibly small (of the order of a few nanometers to a few micrometers). This two dimensional aspect makes it altogether different from its bulk counter part. The surface to volume ratio is higher in thin films than that of bulk. In addition, the average size of crystallites of polycrystalline films is very small. Moreover, various types of defects are present in large amount in thin films.

Intensive investigations are going on not only in the field of applications of thin films, but also in the field of basic studies on thin film physics. Studies on optical, magnetic and electrical properties of films and investigations on structural disorder, phase transition and

various surface phenomena are very important to characterize films for specific industrial and scientific applications [2]. Compactness, better performance and reliability coupled with low cost of production are the driving force for the preference of thin film devices and components over bulk devices.

Studies on semiconducting thin films of copper Chalgogenide materials have received much attention because of their potential application in various solid-state devices such as solar cells, superionic conductors, photodetectors, photothermal converters, electroconductive electrodes, and microwave shielding, etc [3, 4, 5, 6, 7]. The Cu-Te system was first studied in 1907 by Pushkin [8]. He has identified the compounds, Cupric telluride (CuTe) and Cuprous telluride (Cu_2Te). Symko-Davis [9] have reported that the optical band gap of cupric telluride (CuTe) thin films is around 1.5eV at room temperature. It is direct band gap material. From the electron transport study of CuTe material by Newport et al [10], liquid CuTe exhibits metallic behaviour and the sign of its thermoelectric power is positive. The crystallographic structure of CuTe is orthorhombic at room temperature. Many have reported that Cuprous telluride (Cu_2Te) is p-type semiconductor with direct band gap of about 1.12eV [11]. Pathan et al [12] have reported that the optical band gap of Cu_2Te is 2.2eV. The electric properties of thin films of Cu_2Te have been studied by Sorokin [13]. He has reported that Cu_2Te is degenerate semiconductor and the carrier concentration is about $10^{25}m^{-3}$.

The present work focuses on (i) the differential scanning calorimetric (DSC) studies on copper tellurides (ii) the measurement of electrical resistivity and thermopower of bulk materials of copper tellurides (CuTe and Cu_2Te) in the temperatures 80K and 300K (iii) the measurement of electrical resistivity of thin films of copper tellurides from 80K to 300K and (iv) the optical studies of thin films of both compounds using spectroscopic ellipsometry, micro-Raman and photoluminescence measurements.

2 Experimental

CuTe and Cu_2Te alloys purchased from M/s Aldrich (India) with 99.99% purity have been used for preparing thin films by thermal evaporation. A desired amount of material depending on thickness was taken and the entire charge from a molybdenum boat was evaporated under vacuum better than 2 x 10^{-5} mbar on well-cleaned glass substrates of 0.01 x 0.03 m^2. The glass substrates were cleaned with warm chromic acid and distilled water before mounting in the vacuum chamber. CuTe and Cu_2Te thin films of thickness from 50nm to 200nm were deposited. The thickness of the films and the deposition rate were monitored with a Z80 microprocessor based digital quartz-crystal thickness monitor. X-ray diffraction (XRD) measurements were used to determine the structure of the films. The average grain size of the films was determined using XRD and AFM. The surface morphology of the films was studied using SEM and AFM. The chemical composition of the films was analyzed

with EDAX. Thermal analysis of bulk samples has been done between 300K and 575K using differential scanning calorimetry. The electrical resistivity of both bulk and thin films of copper tellurides have been measured between 80K and 300K by linear dc four probe method. The thermopower of bulk samples of copper tellurides has been measured using differential dc method between 80K and 300K. The optical behaviour of thin films of copper tellurides have been studied by spectroscopic ellipsometry method. The lattice vibrations of thin films of these materials have been analyzed by micro-Raman spectrometer. Photoluminescence studies on these films have been carried out in the spectral range from 300nm to 800nm.

3 Results

The phase transformations of copper tellurides have been studied by differential scanning calorimetry in the temperature range from 300K to 575K. The differential scanning calorimetric analysis reveals that there is no phase transition in cupric telluride (CuTe) in the temperature range from 300K to 575K. Mills and Richardson [14] have observed a transition in CuTe at 610K by differential scanning calorimetric measurements. They have found that copper telluride disproportionates to tellurium rich melt and $Cu_{3-x}Te_2$ after 610K. But there are two structural phase transitions in cuprous telluride during heating. The first phase transition is predominent and observed at 456K. The second weak phase transition is at 521K. The nature of phase transitions during

heating and cooling is different. During cooling the second transition is observed at 517K with a small hysteresis of 4K. The predominent transition observed during heating is very weak during cooling and initiates at 445K and it spreads down to room temperature. At room temperature both phases co-exist. Co-existence of both phases has also been observed by Vouroutzis et al [15] and Asodov et al [16].

The thermopower and the electrical resistivity of copper tellurides have been measured between 80K and 300K. The resistivities of both compounds increase with the increase in temperature. The thermopower of these compounds is positive that confirms copper tellurides are p-type. The monotonic increase of thermopower with the increase in temperature indicates that copper tellurides are degenerate semiconductors. The temperature coefficient of resistivity of these materials is calculated and that values are small and decrease with the increase in temperature. This also confirms that bulk materials of copper tellurides are p-type degenerate semiconductors.

Thin films of copper tellurides between 50nm and 200nm prepared by thermal evaporation were annealed at 400K for an hour. It is found by scanning electron microscopy that the surface of the films are smooth and free from void and the grain size of cupric telluride films are larger than that of cuprous telluride thin films. From AFM, the average grain size of CuTe and Cu_2Te thin films of 100nm thickness is 40nm and 27nm respectively, and the surface roughness of thin films of CuTe is 2.9nm and Cu_2Te is of 3.2nm. From XRD measurements, the polycrystalline

nature of thin films and crystallite phases of copper tellurides are confirmed. The crystal structure of CuTe thin films is orthorhombic with a=0.3155nm, b=0.4986nm and c=0.6946nm . The crystal structure of Cu_2Te thin films is hexagonal with a = 0.428nm and c = 0.724nm. The grain size of CuTe and Cu_2Te thin films are also confirmed by XRD using Debey-Sherrer's formula.

The electrical resistivity of annealed thin films of copper tellurides has been measured in the temperature range from 80K to 300K. It is found that the low electrical resistivity of thin films is not only temperature dependent but also thickness dependent. The resistivity of annealed CuTe thin films shows semiconducting behaviour. The electrical resistivity of CuTe thin films systematically decreases with the increase in film thickness. The calculated activation energies of CuTe thin films are different at 80K and 300K and are weakly thickness dependent. The electrical resistivity of Cu_2Te thin films increases with the increase in temperature that indicates that the carrier concentration is almost independent of temperature, i.e, they are degenerate. Sorokin [11] has reported that thin films of Cu_2Te is degenerate semiconductor and its carrier concentration is $10^{25}m^{-3}$.

Spectroscopic ellipsometric data of thin films of copper tellurides have been recorded at room temperature using SENTECH SE850 ellipsometer at 70 degree angle of incidence. CuO model has been found to be the most suitable model the extraction of ellipsometric data of thin films of copper tellurides. Using this model, the spectral dependence of

the refractive index (n), and the extinction coefficient (k) of thin films of copper tellurides have been calculated in the spectral range from 310nm to 800nm. From the spectral dependence of the absorption coefficient, optical bandgaps of copper tellurides have been calculated. It is found that the optical band gap of cupric telluride (CuTe) is thickness dependent and it varies from 1.54eV to 1.62eV. The optical band gap value decreases with the decrease in film thickness. This behaviour is attributed to defects in the films. The real (ε_1) and imaginary (ε_2) parts of the dielectric constant of the CuTe films have been calculated and these values decrease with the increase in photon energy. In cuprous telluride the optical band gap is around 2.2eV. It is independent of the film thickness. This value is different from many of the reported values, but closely agreed with the value reported by Pathan et al [12]. Hence the bandgap of Cu_2Te thin films is also estimated by recording transmittance spectra. It is around 2.2eV and also independent of the thickness of thin films.

The Raman analysis of both bulk and thin films of copper tellurides at room temperature has been carried out. The modes of Raman spectra of bulk and thin films are similar. In cupric telluride (CuTe) thin films, three Raman lines are observed. Among the three Raman lines, the most intense line is observed at 259cm^{-1}. This is due to Te-Te stretching vibration of Te atoms and is assigned to A_1 mode. In cuprous telluride, eight Raman lines have been observed and the high intensity lines are at 145cm^{-1} assigned to A_1 mode (bending), at 215cm^{-1} as-

signed to B_1 mode (antisymmetric stretching) and at 296cm^{-1} assigned to A_1 mode (Symmetric stretching).

The photoluminescence spectra of thin films of copper tellurides are recorded in the spectral range from 500nm to 700nm by exciting with the ultraviolet line of 250nm. The photoluminescence spectra (PL) of thin films of CuTe has a strong peak in the visible region which shifts towards high energy side with increase in film thickness. This might be due to the defect levels present in the thin films. In cuprous telluride, thin films have a peak at 540nm and it is almost at the energy value of 2.2eV. This value is very close to the bandgap value of Cu_2Te determined from spectroscopic ellipsometry and transmittance spectra.

References

[1] Milton Ohring. *The Material Science of Thin Films.* Academic Press,, New York, 1992.

[2] K.Wasa, M.Kitabatake, and H.Adachi. *Thin Film Material Technology.* Springer, 2004.

[3] B.Lio, Y.Xie, J.Huang, Y.Liu, and Y.Qian. *Chem.Mater.*, 12:2614, 2000.

[4] W.S.Chen, J.M.Stewart, and R.A Mickelsen. *Appl.Phys.Lett.*, 46:1095, 1985.

[5] C.Nascu, I.Pop, V.Ionscu, E.Indra, and I.Bratu. *Mater.Lett.*, 1997:73, 32.

[6] H.Okimura, T.Matsumae, and R.Makabe. *Thin Solid Films.*, 71:53, 1980.

[7] M.A.Korzhuev. *Phys.Solid state.*, 40:217, 1998.

[8] N.Pushkin. *Z.Anorg.Allg Chem.*, 56:1, 1908.

[9] M.Symko-Davies. In *Proc. 19th European Photovoltaic Solar Energy Conf.,Paris*, volume 6, 2004.

[10] R.J.Newport, R.A.Howe, and J.E.Enderby. *J.Phys:C.Solid State Phys.*, 15:4635, 1982.

[11] G.P.Sorokin, Yu.M.Papshev, and P.T.Oush. *Sov.Phy.Solid State.*, 7:1810, 1966.

[12] H.M.Pathan and C.D.Lokhande. In *14th AGM and ThemeSymposium on Noval Poymeric Materials*, 2003.

[13] G.P.Sorokin. *Izvestiya VUZ.Fizika.*, 4:140, 1965.

[14] K.C.Mills and M.J.Richardson. *Thermochimica Acta*, 6:427, 1973.

[15] N.Vouroutzis and C.Manolikas. *Phy.Stat.Sol(a).*, 111:491, 1989.

[16] YU.G.Asadov, L.V.Rustamova, G.B.Gasimov, K.M.Jafarov, and A.G.Babajev. *Phase Transitions*, 38:247, 1992.